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OXIDATION STATE ANALYSES OF URANIUM WITH EMPHASIS ON CHEMICAL SPECIATION IN GEOLOGICAL MEDIA

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ABSTRACT

OXIDATION STATE ANALYSES OF URANIUM WITH EMPHASIS ON CHEMICAL SPECIATION IN GEOLOGICAL MEDIA

This thesis focuses on chemical methods suitable for the determination of uranium redox species in geological materials.

Nd-coprecipitation method was studied for the determination of uranium oxidation states in ground waters. This method is ideally suited for the separation of uranium oxidation states in the field, which means that problems associated with the instability of U(IV) during transport are avoided. An alternative method, such as ion exchange, is recommended for the analysis of high saline and calcium- and iron-rich ground waters. $U(IV)/U_{tot}$ was 2.8-7.2% in ground waters in oxidizing conditions and 60-93% in anoxic conditions. From thermodynamic model calculations applied to results from anoxic ground waters it was concluded that uranium can act as redox buffer in granitic ground waters.

An ion exchange method was developed for the analysis of uranium oxidation states in different solid materials of geological origin. These included uranium minerals, uranium-bearing minerals, fracture coatings and bulk rock. $U(IV)/U_{tot}$ was 50-70% in uraninites, 5.8-8.7% in secondary uranium minerals, 15-49% in different fracture coatings and 64-77% in samples from deep bedrock. In the uranium-bearing minerals, $U(IV)/U_{tot}$ was 33-43% (allanites), 5.9% (fergusonite) and 93% (monazite). Although the ion exchange method gave reliable results, there is a risk for the conversion of uranium oxidation states during analysis of heterogeneous samples due to the redox reactions that take place in the presence of some iron compounds. This risk was investigated in a study of several common iron-bearing minerals. The risk for conversion of uranium oxidation states can be screened by sample selection and minimized with use of a redox buffer compound such as polyacrylic acid (PAA). In studies of several carboxylic acids, PAA was found to be the most suitable for extending the application of the method.

The stability of uranium oxidation states during analysis and the selectivity, linearity, repeatability and comparability of methods were examined. Both Nd-coprecipitation and ion exchange were found to be valid and reliable methods. Both are suitable tools for studying oxidation/reduction mechanisms in geochemical processes. The oxidation state analyses of uranium in different geological materials gave new information on the chemical speciation and behaviour of uranium.

ABBREVIATIONS

TTA	thenoyltrifluoroacetone
ICP-MS	induced coupled plasma mass spectrometry
TIMS	thermal ionization mass spectrometry
AAS	atomic absorption spectrometry
PAA	polyacrylic acid (Na-salt)
LA	lactic acid
PAMA	poly(acrylic-co-maleic acid) (Na-salt)
PA	propionic acid (Na-salt)
AA	acrylic acid
XPS	X-ray photoelectron spectroscopy
XAS	X-ray absorption spectroscopy
ADC	analogue digital converter
MCA	multichannel analyser
LLD	lower limit of detection
ANOVA	one-way analysis of variance test

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LIST OF PUBLICATIONS

This thesis is based on the following publications:

I Ervanne, H. and Suksi, J. (1996), Comparison of ion-exchange and coprecipitation methods in determining uranium oxidation states in solid phases. Radiochemistry 38, 4, 306-309.

II Ervanne, H. (2003), Interferences in uranium oxidation states during dissolution of solid phases. J. Radioanal. Nucl. Chem. 256, 3, 497-500.

III Ervanne, H., Detecting and minimizing interferences in uranium oxidation states during dissolution of solid phases, J. Radioanal. Nucl. Chem. (in press).

IV Ahonen, L., Ervanne, H., Ruskeeniemi, T., Jaakkola, T., Blomqvist, R. (1993), Uranium mineral-groundwater equilibration at the Palmottu natural analoque study site, Finland. In: Scientific Basis for Nuclear Waste Management XVI (C. Interrante, R. Pabalan, eds.). Mat. Res. Soc. Symp. Proc. 294, 497-504.

V Ahonen, L., Ervanne, H., Jaakkola, T., Blomqvist, R. (1994), Redox chemistry in uranium-rich groundwater of Palmottu uranium deposit, Finland. Radiochim. Acta 66/67, 115-121.

VI Ervanne, H., Uranium oxidation states in allanite, fergusonite and monazite of pegmatites from southern Finland, N. Jb. Miner. Abh. (in press).

The publications are hereafter referred to by their Roman numerals. The first three papers (I, II, III) treat the development and testing of methods for the analysis of uranium oxidation states in geological phases. The application of the methods to groundwater is presented in papers IV and V. Analyses of solid samples are discussed in papers I, III and VI. Paper VI presents the results of determinations of uranium oxidation states in radiation damaged, metamict minerals. The summary contains also results not published earlier.

1. INTRODUCTION

1.1 Background

A thorough understanding of chemical speciation is necessary if the behaviour of a radionuclide is to be properly described and predicted. Species are the specific forms of an element, differing in oxidation state and formal charge and exhibiting characteristic chemical reactivity and stability. Speciation analysis refers to the analytical techniques used in identifying and quantifying these species.[1]

Uranium has two oxidation states, U(IV) and U(VI), that are geochemically relevant. The third valence state, U(V), is of only minor importance. The chemical behaviour of U(IV) and U(VI) under environmental conditions is influenced by a variety of reactions, including dissolution, precipitation, complexation and sorption. All these reactions are affected by redox conditions, pH, water composition and water-mineral interactions. Uranium shows distinct geochemical properties in its two oxidation states. A change in environmental conditions may immobilize the soluble U(VI) through reduction to sparingly soluble U(IV) or, reversely, mobilize U(IV) through oxidation to U(VI).

The physico-chemical properties of uranium are of continuing interest because uranium is a major constituent of highly radioactive spent nuclear fuel, which must be disposed of safely. Under reducing conditions the release of uranium from an underground repository is controlled by the solubility of uraninite, UO_2. It has been suggested that Fe(II) could be added to the back-fill material as a reductive additive to isolate uranium more effectively within a multibarrier system.[2] In the surrounding rock of a disposal site the reductive capacity of the rock is a crucial parameter in hindering uranium migration along the water path.

Glass and ceramic hosts are two waste forms currently under consideration for permanent disposal of radioactive high level waste. Although radiation effects on the stability and durability of these hosts have been actively investigated,

radiation damage processes are not yet well understood. Ceramic materials hold reduced species of actinides in their structure very well, but radiation damage, accompanied by a change in environmental conditions, could cause oxidized uranium to leach out.[3,4] Metamictic minerals like zircon, monazite and pyrochlore have been used as natural analogues in the study of radiation damage effects.[5,6]

The remediation of areas contaminated by the nuclear fuel cycle is an important part of environmental protection policy. In many countries, intensive uranium mining and milling have caused environmental pollution.[7-9] Agricultural drainage waters constantly released to the environment may be a source of radioecological contamination.[10] Purification of large volumes of contaminated water requires economically attractive technologies. The information obtained on uranium oxidation states can be utilized in remediation of ground water and the restoration of contaminated areas. For instance, a permeable treatment zone can be created by metallic iron or microbes to accomplish the reduction of uranium to less mobile form, thereby preventing contamination of surrounding areas.[9] Modelling of the environmental migration of uranium relevant to possible releases associated with nuclear disposals and other sources requires detailed prediction of speciation distributions.

1.2 Scope of the study

Effective methods are required to study the redox speciation of uranium in complex geological matrices. Methods available to determine uranium oxidation states include both non-destructive methods and chemical separation procedures. Common chemical separation procedures are based on coprecipitation,[11-14] ion exchange[15-17] and solvent extraction.[18-21] Although the methods are well established, there is a lack of information on the behaviour of elements, that may interfere with the uranium oxidation state distribution during analysis.

The general aim of the present work was to investigate chemical methods for determining uranium oxidation states in different geological materials.

Two methods, one based on Nd-coprecipitation and one on ion exchange, were of interest. The effects of interfering elements or compounds, especially iron-bearing compounds, on the determination of uranium oxidation states of solid phases can be profound. Effects of common iron-bearing minerals were accordingly studied in some detail. In addition, compounds were sought that might prevent redox reactions of these interfering compounds from occurring during the analysis of uranium oxidation states.

1.3 Properties and occurrence of uranium

There are three isotopes of uranium in nature. ^{238}U and ^{235}U are the parent isotopes for two separate radioactive decay series and ^{234}U is formed by decay in the ^{238}U-series. The intermediate nuclides are ^{234}Th and ^{234}Pa (Table 1). The main oxidation states of uranium in nature are IV ($[Rn]5f^2$) and VI ($[Rn]5f^0$); oxidation state V ($[Rn]5f^1$) occurs only rarely. U(IV) exhibits chemical similarities with other actinides with oxidation state IV, while U(VI) follows the behaviour of actinides with oxidation state VI.

Table 1. The properties of natural and artificial uranium isotopes.[22-24]

Isotope	Alpha energy (MeV)	Intensity (%)	Half-life (a)	Abundance (%)
^{238}U	4.198 4.151	79 21	$4.47*10^9$	99.27
^{235}U	4.398 4.366	57 17	$7.04*10^8$	0.72
^{234}U	4.775 4.722	71 28	$2.45*10^5$	0.0055
^{232}U	5.320 5.264	68 32	71.9	-
^{233}U	4.824 4.784	84 13	$1.59*10^5$	-

Occurrence in water

Uranium in freshwater and sea water usually occurs in U(VI) form; exceptions are possible in anoxic basins where uranium may be present in reduced form as well.[25-27] Uranium exists in U(IV) or U(VI) oxidation state in ground water

depending on the environmental conditions. The U(VI) state is highly soluble, unlike U(IV) which is sparingly soluble. Uranium concentration in water varies enormously, from 0.1 µg/l in reducing conditions to as much as several grammes per litre in oxidizing conditions. The average concentration in sea water is 3.3 µg/l and in surface waters 0.01 to 5 µg/l. In ground water the concentration typically ranges from 0.1 to 500 µg/l.[28]

According to Bruno et al.[29] the dissolved U(IV) in natural waters ranges from 3 to 30 µg/l. Dissolved U(IV) concentrations are an order of magnitude higher in Na-K-Ca-Cl brines than in fresh waters.[30] Anaerobic systems with high carbonate alkalinities or high dissolved organic matter concentrations may contain more soluble U(IV) than currently thought.[10] U(IV) concentrations measured in sea water have been lower than predicted from thermodynamics.[11,26] In contact with reducing sediments the uranium in water may be reduced.[31,32]

Uranium species in natural waters

Uranyl ion UO_2^{2+} behaves like divalent metal ions of smaller size (or the same size, but higher charge). Carbonate is the most significant uranium ligand in natural water and the greater solubility of the U(VI) ion is in part due to its tendency to form anionic carbonate complexes.[33] Figure 1 shows the dependency of the speciation distribution on pH and carbon dioxide concentration in a closed system. The formation of carbonate complexes can change the stability field of U(VI). These U(VI) complexes may exist in alkaline conditions and high carbonate concentrations even in reducing conditions.[34]

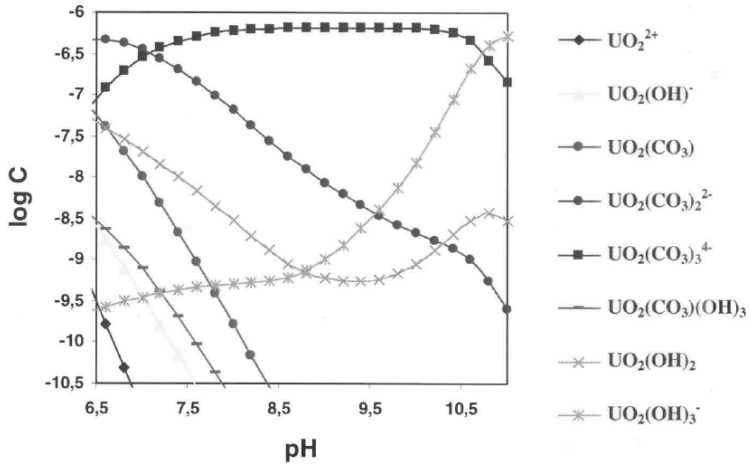

Figure 1. The effect of pH and concentration (log C, M) of carbon dioxide on the speciation of uranium in ground water assuming a closed system. The species were calculated by the HYDRAQL program[35] for sample 302/90-95m.(**V**)

Uranyl hydroxy complexes such as UO_2OH^+ and $(UO_2)_3(OH)_5^+$ are also formed, but generally in smaller amounts except at high temperature or in carbonate-depleted alkaline water. In reducing water, the U(IV) hydrolysis product is $U(OH)_4^0$. Other possible complexes are formed with SO_4^{2-}, PO_4^{2-}, Cl^- and F^- ions. Complexation may also be important with humic substances.[33] The solubility of reduced uranium is low and it has a strong tendency to hydrolyse, easily forming colloids, especially when environmental conditions change. High concentration of inorganic salts hinders the formation of colloids, and colloids already present may coagulate.[36]

Distribution in rocks and minerals

Common major minerals have very low uranium content, which means that the common rocks contain uranium in only low concentration. As an example, the concentration of uranium in granites is normally about 4-5 mg/kg. The concentration in granitoids varies more widely between 0.1 mg/kg and 30 mg/kg. The distribution of uranium in sedimentary rocks is difficult to summarize, but black shales, phosphate rocks and coal often have very high uranium contents. Metamorphic rocks have approximately the same uranium contents as the protoliths they derive from.[37] Uranium oxidation states in rocks vary

with the reductive capacity of the rock, which usually is determined by the iron minerals present. The more oxidizing water-rock interaction there has been, the more uranium is in oxidized state. Uranium oxidation states have been determined in various rock types and great variation has been found, as expected.[38] The amount of reduced uranium U(IV) in the nodules of sea-floor deposits ranges from 56 to 96% of total uranium.[39]

Uranium may be a major element in a mineral, for example uraninite UO_{2+x} ($0<x<0.25$), or it may be present as an accessory element. Some common accessory minerals such as thorite $(Th,U)SiO_4$ and uranothorite $(Th,U)SiO_4$ (~1-35 wt% UO_2) incorporate uranium in their structure and may contain appreciable amounts.[37] The different oxidation states of uranium are incorporated according to the characteristic properties of each oxidation state and the properties of the mineral. In apatites, $Ca_5(PO_4)_3(OH,F,Cl)$, for example, uranium is emplaced solely as U(VI), substituting for Ca(II) in the crystal structure.[14] In calcites, $CaCO_3$, on the other hand, uranyl ion is too large for the regular lattice sites and U(IV) is substituted instead. [40]

The U(IV) minerals contain regular coordination polyhedra about the U^{+4} cation, and tend to have high symmetry. U^{+4} tends to substitute for other cations in a variety of mineral structures, and the minerals are commonly isostructural with non-uranium analogues. Often these minerals are more complex owing to the tendency of some U(IV) to oxidize. In addition, substitution of elements such as Th(IV) and REE(III) for U(IV) is common.[41]

The most important U(IV) mineral is uraninite, of nominal composition UO_2. The oxidation state distribution in uraninites varies with rock type. For example, the mean oxidation state of uranium is generally lower in pegmatitic uraninites than in vein and sedimentary uraninites.[42] The oxidation state distribution also affects the behaviour of the mineral. Although uraninite is nominally UO_2 in composition and it possesses the fluorite structure, it always shows a higher degree of oxidation. Once it is oxidized to $UO_{2.25}$, for instance, it seems to be stable in air for long periods of time at ambient conditions. There is no simple correlation between the oxidation state of uranium in

uraninite and unit-cell size.[43]

Most U(VI) minerals involve the nearly linear uranyl ion UO_2^{2+}. Oxidized minerals are usually hydrated oxides, silicates and phosphates, but minerals of all groups may occur. The structures of U(VI) minerals are diverse and the minerals are seldom isostructural with other minerals.[41] The most common uranyl minerals are uranophane, $CaUO_2SiO_3(OH)_2 \cdot H_2O$, and autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 10\text{-}12H_2O$. In oxidation state VI, uranium may deposit in the oxidized zone associated with a primary deposit or it may be transported with water a considerable distance from its source area before reprecipitation.

1.4 Redox concepts

An element or ion loses electrons in oxidation and receives them in reduction. In oxidation its oxidation state increases and in reduction it decreases. This change in state can be written as half reactions

$$A^z \rightarrow A^{z+a} + ae^- \quad (1)$$

$$B^{z+b} + be^- \rightarrow B^z \quad (2)$$

where A^z is an ion with valence state z, e^- is an electron, and a and b are the number of electrons taking part in the reactions.

Oxidation is always accompanied by reduction, and vice versa. Redox reactions always occur in pairs and usually the redox pairs are presented in the form of a single reaction, a redox reaction:

$$bA^{z+a} + aB^z \rightarrow bA^z + aB^{z+b} \quad (3)$$

Thermodynamically, the redox potential E (also designated Eh) of the solution and the activities of the reduced and oxidized ([red]/[ox]) species are expressed by the Nernst equation

$$E = E_0 + \frac{RT}{nF}\ln\left(\frac{[ox]}{[red]}\right) \quad (4)$$

where R is the gas constant, T the temperature (^{0}K), n the number of electrons transferred, F the Faraday's constant and E_0 the standard redox potential. In equilibrium, when E=0, the equation can be written as

$$E_0 = \frac{RT}{nF}\ln K \quad (5)$$

where K is the equilibrium constant for the reaction. Complex formation affects the standard potential.[44] In many redox reactions, hydrolysis of the redox-active species is involved and the redox potential value is then dependent on the hydrogen ion activity (pH) of the solution.

Reducing or oxidizing capacity of a system is expressed as the number of electrons that are needed or that must be removed to obtain a certain redox potential in the system. The oxidizing capacity of the system in respect of a certain energy level of electrons can be obtained from summing all the oxidants below this level and subtracting all the reductants above this level. Reductive capacity [RDC], which describes the ability of a system to resist a change in the redox potential, is expressed by the following formula:

$$[RDC] = \sum_i \{n_i [red]_i\} - \sum_j \{n_j [ox]_j\} \quad (6)$$

where [red] and [ox] describe activities of the individual reductants and oxidants, while n_i and n_j are the number of equivalent electrons transferred in the reaction.[45] For example, uranium close to uranium mineralizations and iron minerals can be redox-controlling phases in deep granitic ground waters.[46,IV]

The redox potential in solution can be measured with a redox electrode (Pt, Au or C) in combination with a reference electrode such as a standard hydrogen electrode or Ag/AgCl. The redox electrode develops a potential proportional to the ratio of the redox species in the solution. In natural systems there may be more than one redox pair, in which case the measured Eh reflects the

mixture of prevailing redox species. Several factors are reported to affect Eh measurements.[47,48] In deep ground waters Eh can be measured with a precision of ±(25-30)mV.[8,49] Another way to determining the redox potential is to measure the concentrations of the different redox species.

Several thermodynamic databases and computer codes are available to calculate the speciation of uranium for purposes of geochemical model calculations.[50-52] From these, Eh-pH diagrams can be drawn, which show the relative stability fields of the mineral phases or uranium species present in water. In Figure 2 the measured values close to the phase boundary show the dominant redox system. These models describe the equilibrium conditions, however, which are not always attained in ground waters. Indeed, there has been some debate over the use of the equilibrium concept to define redox reactions in natural systems.[45,53] There may be more than one redox pair in natural systems, and often these pairs are not in equilibrium. In that case it may be difficult to establish which controls the system. Furthermore, a larger amount of quantitative information than presently exists on formation constants for U(IV) hydrolysis and carbonato species is required to obtain model results that are in agreement with laboratory or field measurements.[50,54-56]

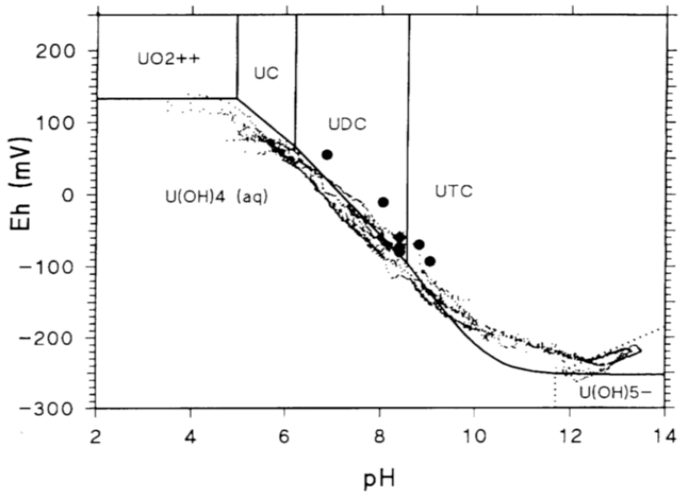

Figure 2. Eh-pH diagram showing the prevailing redox pairs at the Palmottu natural analogue site. UC, UDC, UTC denote uranyl mono-, di- and tricarbonates, respectively.(**V)**

The oxidation state of uranium may change if the redox conditions of the environment change (through introduction of oxygen, sulphide, organic matter or bacteria or contact with mineral surfaces). Decomposing organic matter creates anaerobic conditions, which promote the chemical or biological reduction of uranium.[39] Natural humic acids in peat bog, Fe-reducing bacteria in sediments and organic matter in general have been reported to induce uranium reduction.[31,57] Changes in chemical state subsequent to radioactive decay are well known in hot atom chemistry. ^{238}U can eject alpha recoil ^{234}Th, which rapidly decays to ^{234}U. It has been suggested that this uranium atom may then end up in an unusual lattice position or in ground water, which favours its oxidation.[58,59] Radiation damage in a mineral may alter its structure and uranium oxidation state distribution. Auto-oxidation, where the decay product Pb^{+4} as a strong oxidant oxidizes the uranium, plays a significant role in oxidation state distribution when the sample is very old.[43] These radiation damage processes can effectively be studied in metamictic minerals.

2. METHODS TO DETERMINE URANIUM OXIDATION STATES

2.1 Sampling and pretreatment

In chemical speciation analysis, particular attention must be paid to conditions during the sampling to ensure minimal interference with the oxidation state distribution. In particular, contact with oxygen should be avoided. When oxidation states are separated in the field, the disturbances possible during transport from field to laboratory are avoided.

Ground water

Ground water samples are preferably collected with a double packer system.[60] Water samples taken with this equipment are more representative than those taken by tube sampling technique. The double packer system consists of hydraulically expandable rubber packers, which isolate the water conducting fracture of the drilling hole to be sampled. With the fracture sealed off from the surrounding rock, changes in flow direction and mixing processes are effectively prevented, so that the water represents the original fracture water. Sequential pressure pulses are regulated with nitrogen gas and the water is forced to flow out from the airtight sampling tube. The water is led to a flow-through cell in which Eh, pH, dissolved oxygen and electric conductivity (EC) are measured. Water is collected from a parallel outlet. Protective nitrogen or argon gas flow helps to keep oxygen out of the collecting system.

Solid samples

In the collection of solid samples, the use of water should be kept to a minimum. Samples should be as homogeneous as possible. All uranium should be obtained in soluble form before the separation of uranium oxidation states by chemical methods. The rate of dissolution depends on the oxidation state of the elements, the mineral structure, the site of the element in the mineral, bonding, and complex-forming ligands. Aggregation properties, such as found with smectite, will hinder the dissolution of uranium.[61] Concentrated mineral acids have often been used for dissolving purposes, but less aggressive reagents should be preferred whenever possible.

2.2 Chemical separation of oxidation states

There are two approaches to determining the oxidation states of uranium. In the first, the amount of total uranium and U(VI) species are determined and the amount of U(IV) species is calculated as the difference. In the second, U(VI) and U(IV) concentrations are determined directly. Several methods for the quantitative determination of uranium in coexisting oxidation states have been described in the literature. Common chemical methods are coprecipitation,[11-14] ion exchange[15-17] and solvent extraction.[18-21] These chemical methods will now be discussed.

Coprecipitation

In coprecipitation, trace amounts of radioelements are incorporated in a precipitating solid. One of the earliest methods employed was coprecipitation with cupferron (ammonium nitrosophenylhydroxylamine) from acid solutions such as H_3PO_4, H_2SO_4 and HCl.[12] The U(IV) is found in the precipitate, while U(VI) stays in solution. Later, cupferron was replaced by lanthanides such as neodymium and cerium as a carrier.

Coprecipitation with lanthanides is a well characterized actinide separation method. The method takes advantage of the strong complexation of fluoride solely with reduced ions (III, IV), the insolubility of the neutral fluoride compounds, and the slow redox kinetics between the reduced and oxidized (V,VI) states.[62] The separation procedure for uranium oxidation states is based on the coprecipitation of U(IV) with LaF_3 in slightly acidic solutions while U(VI) stays in solution. A detailed description of the coprecipitation method as applied to the determination of uranium oxidation states in natural waters is given by Anderson.[11] The method has been modified by Leskinen[63] and Suutarinen et al.,[64] who apply Sill's[65] method for the lanthanide coprecipitation in preparing the measuring preparate. The coprecipitation method provides rapid separation of oxidation states from a large volume of water in field conditions. A disadvantage is the requirement for use of a lower pH than that of the original water.

Ion exchange

Ion exchange is a reversible reaction where the counter ions on a resin are exchanged for dissolved ions of the same electric charge in solution. Kraus et al.[17] demonstrated almost 50 years ago that ion exchange chromatography is suitable for uranium speciation. They found that U(IV), unlike U(VI), is readily eluted from strong base anion exchange resin at high concentrations in HCl media, and also in the presence of small amounts of HF. The resin was composed of $-NR_3^+$ functional groups, with which uranyl ions form strong anionic chloride complexes. Hussonois et al.[16] modified the basic ion exchange separation method for water samples by adsorbing U(VI) to the resins from 4.5 M HCl solution under conditions in which U(IV) quantitatively passed through the column. The pH, or the chloride concentration in the case of saline waters, may have to be adjusted to obtain a solution suitable for ion exchange.

As well, chelation ion chromatography has been successfully applied.[66] Other kinds of resin, such as latex-based cation exchange resin carrying negatively charged sulphonate functional groups have been used.[67] A method for saline and high carbonate waters, was developed by Duff and Amrhein,[68] in which a low pressure chromatographic separation with a cation exchange resin was combined with ICP-MS (Induced coupled plasma mass spectrometry). The separation of oxidation states was based on different, ion characteristic, elution times of tetravalent and hexavalent uranium. Interferences were observed at 2 g/l calcium concentrations.

The disadvantages of chromatographic methods include the need in most cases for low pH values and the need for preconcentration of samples of low activity to allow loading on the column in small volume. Handling large volumes of ground water then becomes awkward and time consuming.

Solvent extraction

Solvent extraction is a reversible process where metal ions in water solution form complexes with an organic extractant and are removed to the organic phase. Solvent extraction provides a rapid and basically complete separation of oxidation states. Various organic solvents are available for extraction.[18-21]

A commonly used solvent for uranium is thenoyltrifluoroacetone (TTA), which extracts U(IV) while leaving U(VI) in water solution. U(IV) is then back extracted. Extraction with TTA has one basic limitation: aqueous phase solubility increases above pH 4, limiting its use to acidic media. A pH adjustment may thus perturb the redox equilibrium.[62] As in the traditional ion exchange method, handling of large volumes of ground water is impractical.

2.3 Measuring techniques

Uranium in chemically separated oxidation state fractions uranium can be measured by alpha spectrometry, mass spectrometry or other spectrometric method.[69] There are also spectrometric methods, that measure U(VI), and total uranium, after which the U(IV) is determined indirectly from the total uranium concentration. Each method has its advantages and limitations. Determination of the oxidation states of chemically complex systems often requires the use of several techniques, usually including chemical separations. With the development of modern techniques, the limit of detection has fallen to such low levels that even a minor contamination during sample manipulation poses a problem.

Alpha radiation from a nuclide has a characteristic energy spectrum by which it can be identified if the energy resolution of the detector is sufficient. Alpha spectrometry is widely used to measure uranium and other actinides. Relative to ICP-MS, the instrumentation is of relatively low cost. Other advantages are low background, which translates into high sensitivity, and the possibility to obtain isotopic ratios in a single measurement. The sensitivity is not as good as for ICP-MS, however, and much poorer than that of Thermal ionizations mass spectrometry (TIMS).[67,70-71]

Separated uranium oxidation states are regularly measured by ICP-MS, down to 10^{-9} M in solution.[67,71] Unfortunately, the new organic resin and extractant materials tend to produce negative side-effects in ICP-MS analysis. And matrix effects may affect the precision of the determination. These effects can be reduced either by dilution or by the standard addition technique. At

concentration levels below 10^{-7} M the uncertainty of the analysis is reportedly about 3%, increasing if chemical manipulation is necessary.[8] Below 10^{-7} M precision will be reduced by the need for sample pretreatment. In many cases, chemical separation is essential to provide optimal ionization efficiency or signal to noise ratio.

Laser spectroscopy has established its position among techniques useful for speciation analysis of uranium in aquatic samples. Various methods capable of characterizing oxidation and complexation states of uranium ions have been introduced.[7,72] U(VI) is easily measured in higher concentrations by spectroscopic techniques, in optimum conditions and by laser induced fluorescence spectroscopy down to 10^{-10} M. However, there may be interferences, especially from Fe^{+3}, and manipulation of the sample is needed in the analysis of low-level environmental materials.[8]

There are also several spectroscopic techniques for solid materials. XPS (X-ray photoelectron spectroscopy)[73,74] and XAS (X-ray absorption spectroscopy)[10,75] are the most frequently used for uranium speciation. Both techniques are non-destructive, requiring no chemical preparation, and they can be used to study the composition of both crystalline and amorphous solids. Both are surface analytical methods. Spectra provide information about the oxidation states of elements, their surface complexation and their coordination environment. XPS can provide structural information on the environment of elements to a depth of 5 to 10 nm.[76,77] The accuracy of XPS for solid surfaces is reported to be within 1% and that of XAS within 6%.[2,73] The limit of detection for uranium is reportedly about 1 mg/g for XAS.[78] Although XPS is generally considered a non-destructive technique, changes in the surface of the sample have occasionally been noted. Reduction of transition metals in maximum valency compounds has been found, for example.[79,80]

2.4 Interferences occurring during separation of oxidation states

Many analytical methods do not allow reliable results for all sample types. Unwanted interfering reactions sometimes occur during analysis. Clearly,

interference is more serious when elements acting as oxidizing or reducing agents towards uranium are present in quantities comparable to or greater than uranium. A reduction in pH during sample analysis may intensify interference reactions. In this work uranium oxidation states in ground water were determined by Nd-coprecipitation. For solid phases, ion exchange method after dissolution of the sample was used as well. Some of the problems associated with these methods are examined below.

Nd-coprecipitation method

In water samples analysed by Nd-coprecipitation method, the U(IV) fraction is coprecipitated with neodymiumfluoride (NdF_3) from dilute HCl solution. Recoveries are typically over 99%. During coprecipitation, however, several ions may compete for fluoride and the available coprecipitation sites. Sill[81] did thorough work on this subject and in his view, the fluoride system suffers from severe interference from such common elements as aluminium, calcium and magnesium. With larger quantities of uranium the presence of these elements leads to sharply decreased yields and degraded alpha spectra. Once the available lattice positions in the carrier are used up; the precipitation of uranium falls off abruptly for the excess uranium does not precipitate by itself.[81]

Radium isotopes also tend to coprecipitate in this procedure. Although Sill was unable to give exact concentration limits for these elements in solution, their interference can be observed in yields and spectra. Where there is interference, the method can then be replaced by another or the poorly behaving sample can be rejected.

Although the interference due to aluminium, calcium and magnesium are not well understood, presumably they are associated with isomorphous replacement in the NdF_3 lattice because the charge or ionic radius is close to that of Nd. It is not clear, however, which element or elements help to maintain the charge neutrality. In the case of radium the ionic radius is far larger than that of the interfering elements and the mechanism for coprecipitation is different. A badly degraded alpha spectrum is most likely due to precipitation

of the sparingly soluble sodium salt of the fluoride-aluminium complex.[81] For its part, a large quantity of calcium can mask a small amount of uranium so that the precipitation of reduced uranium is incomplete. Duff and Amrhein[68] report that over 0.4 g/l Ca concentration can perturb the analysis. The interferences are due to the low concentration of Nd that is used relative to the concentrations of other elements.

In the presence of high concentrations of fluoride and acid, Fe(II) tends to become a particularly powerful reducing agent and may reduce part of the uranium. The reduction potential of iron is dramatically increased by the strong complex formation between fluoride ion and iron in the oxidized state.[81] As a result, iron-rich waters cannot be analysed for uranium oxidation states by the Nd-coprecipitation method. A high content of iron may also disturb determination of the U(VI) fraction. In U(VI) analysis uranium is reduced with $TiCl_3$, and if the reducing capacity of $TiCl_3$ is consumed by iron, the reduction of uranium will be hindered. An extremely low yield is obtained as a result. When waters with high fluoride concentration are to be analysed the amount of fluoride reagent should be decreased.

Dissolving of solid phases

Basic strong anion exchange resin is widely used in the separation of uranium from other elements owing to its high selectivity and capacity. Since its suitability for a variety geological matrices is well established, it is not discussed here. The interfering effect of the heterogeneity of solid samples, especially samples containing iron, which can act as reductant or oxidant, is worth examining, however.

Problems may arise in the analysis of solid materials right at the beginning when the sample is dissolved. By way of example, let us consider two types of sample. In the first type of sample, uranium and iron in their different valence states are evenly distributed and the element distributions and redox conditions can be considered as homogeneous. The oxidation state data obtained from this kind of sample represents the original situation. In the second type of sample, the two elements are unevenly distributed, which can mean heterogeneity in

elemental composition or in oxidation state distribution. For example, there may be coarse-grained iron-rich minerals in aggregates or there may be a clear redox front. When the sample is dissolved as a whole, the different redox phases are mixed and the result does not necessarily describe the oxidation state distribution in the original sample.

When an iron-containing sample is dissolved the iron that is released may be in oxidation state II or III depending on the solid phase from which it has dissolved. Release and oxidizing or reducing capability of iron greatly depend on its form, compound and location. In sulphide FeS_2, iron exists in oxidation state II, whereas in biotite $K(Mg,Fe(II))_3(Al,Fe(III),Si_3,O_{10})(OH,F)_2$, part of it may be present in higher oxidation state III. Various redox reactions are likely to occur if any element capable of shifting the redox potential of the solution is acting as reductant, oxidant or catalyst. Such reactions could cause an unacceptable change in the uranium oxidation state distribution.

Few studies have examined the interferences that may arise in determining uranium oxidation states. The ability of iron-containing minerals to reduce or oxidize uranium in contact with ground water has been investigated only in the neutral region, but the results suggest what may occur in acidic solution. Common rock minerals such as magnetite $Fe(II)Fe_2(III)O_4$,[77,82] chlorite $(Fe(II),Mg,Fe(III))_5Al(Si_3,Al)O_{10}(OH,O)_8$,[83] biotite,[84] hematite Fe_2O_3[85] and pyrite[86] have been investigated. The ability of a high-FeO olivine-rock to reduce uranium has also been reported.[2] These findings suggest that pyrite, the most common sulphide mineral, is a powerful reductant, whereas the other minerals act more slowly in changing the redox potential to oxidize or reduce uranium, and complete reduction or oxidation is not necessarily achieved. According to Clarke Jr and Altschuler,[14] in materials containing over ten per cent of iron, the iron may change the oxidation state of uranium in slightly acid solution. Fattahi and Guillamont[15] report on the basis of studies on solid hematite that small amounts of Fe(III) are tolerated.

Preventing interference during dissolution

Only a few compounds – hydrazine and some polyelectrolytes such as lactic and malonic acids – have been tested as agents to eliminate or at least minimize

the interfering effects of iron.[14,15,87,88] In aqueous solution the reduction of metal atoms by electrons is strongly inhibited when the cations are held in the potential fields of negatively charged polyelectrolytes or micelles.[89-91] Carboxylic groups can associate with metal ions, notably alkaline earths and transition metals such as iron, and act as a metal ion buffer.[92] Oringer et al.[87] and Millner et al.[88] used polyelectrolytes to form complexes with Fe(III) salts in solution to prevent them from disturbing uranium determinations. Later Clarke Jr and Altschuler[14] studied the use of hydrazine to stabilize the redox conditions. Unfortunately, some of the samples behaved exceptionally and were not stabilized. No ideal redox buffer is known at present. A redox holding agent is nevertheless required when uranium oxidation states are determined in complex geological material.

3. EXPERIMENTAL

3.1 Reagents and samples

Reference material for oxidation state studies (papers **I,II,III**)

After testing of the methods, it was assumed that the separation of oxidation states in ground water was quantitative and specific tracers for oxidation state were not employed. Synthetic UCl_4 was used as reference material in the first experiments with solid phases. Although originally totally in reduced form, UCl_4 is easily oxidized, however, and a low-grade uranium ore material, DL-1a, was preferred as reference and testing material in later experiments.[93] The DL-1a material was a homogenized powder with grain size below 74 μm and main minerals uraninite UO_{2+x} ($0<x<0.25$) and brannerite $(U,Ca,Ce)(Ti,Fe)_2O_6$. The uranium concentration of 0.0166 ± 0.0003 wt% is reported.[93] The oxidation state data of DL-1a was determined by ion exchange and Nd-coprecipitation methods, and U(IV) represented 56% of the total uranium.

Iron-bearing minerals in interference studies (**II,III**)

Common natural iron-bearing minerals representing different oxidation state distributions were used in the interference studies (Table 2). The minerals were in homogenized powder form (<1 mm). The total iron content was determined by ICP-MS and the Fe(II) content by titration from silicates.

Table 2. Natural iron-containing minerals used in interference studies.

Mineral	General formula	$Fe(II)/Fe_{tot}$ (%)
Pyrite	$Fe(II)S_2$	100
Biotite	$K(Mg,Fe(II))_3(Al,Fe(III))Si_3O_{10}(OH,F)_2$	13
Hornblende	$(Ca,Na)_{2-3}(Mg,Fe(II),Fe(III),Al)_5(Al,Si)_8O_{22}(OH)_2$	10
Chlorite	$(Fe(II),Mg,Fe(III))_5Al(Si_3Al)O_{10}(OH,O)_8$	4
Goethite	Fe(III)OOH	0

Reagents in interference studies (**III**)

Hydrazine monohydrochloride and different carboxylic acids were used in the interference studies (Table 3). The acid concentration was 1% in the screening tests and up to 5% in further tests. Hydrazine was 1.5% solution. Carboxylic acids and hydrazine were diluted into 4.5 M HCl + 0.03 M HF medium.

Table 3. Reagents used in the interference studies (M_w is the weighted average of molecular weight and M_r is the relative molecular mass).

Abbr.	Acids	Formula	M_w or M_r
Hydrazine	Hydrazine monohydrochloride	$NH_2NH_2 \cdot HCl$	68.51
PAA	Polyacrylic acid (Na-salt)	$[-CH_2CH(COOH)-]_n$	1 200
LA	Lactic acid	$CH_3CH(OH)CO_2H$	90.08
PAMA	Poly(acrylic-co-maleic acid) (Na-salt)	$[-CH_2CH(CO_2H)]_x \cdot [-CH(CO_2H)CH(CO_2H)]_x$	50 000
PA	Propionic acid (Na-salt)	CH_3CH_2COOH	96.06
AA	Acrylic acid	$CH_2{:}CHCO_2H$	72.06

Ground waters (**IV,V**)

Ground water samples were collected from uranium-thorium deposit at Palmottu in Southern Finland, which has been used as a natural analogue site in nuclear waste disposal studies.[94,95] Double packer equipment was used to isolate water conducting fractures in drill holes and to pump the representative water samples.[60]

A protective gas flow was applied during pumping and immediately upon arrival at the surface the water was conducted through a 0.45 µm prefilter to the reaction vessel. At the same time Eh, pH, dissolved oxygen and EC were measured.

Seven waters were analysed by Nd-coprecipitation method for uranium oxidation states, and the other waters were used for testing purposes. The water samples represent different types of water and redox conditions. Their chemical compositions are presented in Table 4. Figure 3 shows the locations of drill holes from which samples for uranium oxidation state analysis were taken.

Solid phases (**I,II,III,VI**)

The solid samples can be divided into five groups: 1) uraninite, 2) secondary uranium phases, 3) fracture coatings, 4) bulk rock material, and 5) uranium-bearing minerals. The samples are described in Table 5.

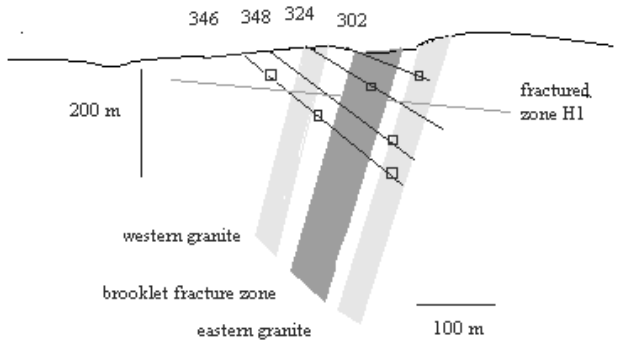

Figure 3. Vertical cross-section (SW-NE) showing the location of drill holes at Palmottu, Finland, that were analysed for oxidation state. (Modified after Ahonen et al. 1994). (**IV**)

Table 4. Chemical composition of ground water samples from Palmottu, Finland (TDS is total dissolved solids).[96]

Drill hole	Depth (m)	^{238}U (µg/l)	Na (mg/l)	K (mg/l)	Al (µg/l)	Mg (mg/l)	Ca (mg/l)	Fe (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)	Cl (mg/l)	TDS (mg/l)
302	80-131	93.8	25	0.92	6.16	2.77	11.3	0.05	10.5	85.4	1.36	142.7
302	90-95	156	17.2	1.11	26.7	4.55	18.5	0.09	13.3	100	2.1	163.1
318	50-80	89.5	34.4	2.18	13.4	3.11	18.1	0.06	20.8	116	6.45	207.1
324	95-101	59	13.4	1.4	110	4.7	31	2.81	17.6	107	4.3	191.3
324	175-200	35.9	38.6	1.3	-	2.2	19.7	0.08	55.0	95.0	3.2	220.0
346	65-71	78.1	12	2.5	90	7.4	34.6	0.05	14	140	3.1	219.0
346	122-128	11.8	53.2	1.89	25.1	7.68	21	0.03	33.8	165	21.5	310.2
346	240-246	1.26	416	2.9	44.7	4.77	26.5	0.02	794	57.4	72	1380
348	200-225	2.5	430	2.03	77.7	4.85	24.8	0.05	580	75.7	71.3	1195
357	165-171	5.68	63.3	3.1	-	6.3	21.6	<0.04	32.0	107	55.0	290.0
384	57-94	87.8	3.54	1.5	6.5	3.64	21.4	<0.03	7.92	73.2	1.30	117.3
385	217-223	0.57	75.8	0.90	916	0.56	1.68	0.83	4.91	128	41.8	264.0
385	403-409	0.27	481	5.25	90	15.6	87.3	<0.05	51.1	31.7	855	1540
387	304-339	1.56	506	3.0	71.7	14.9	39.4	0.07	747	54.9	315	1687

3.2 Procedures

3.2.1 Pretreatment of tracers and samples

Distilled water and p.a.(pro analysis) chemicals used in analyses were treated with argon or nitrogen gas to remove free and absorbed oxygen. All procedures were carried out in a protective gas flow.

Table 5. Analysed solid materials and their site descriptions (for references see text).

Type	Sample	Material	Source
1	A9645	Uraninite	Joachimsthal, Czech
	DL-1a	Uraninite, brannerite	A certified U-Th reference ore, Canada
	304/15.1	Uraninite, U-silicates	Drill hole 304, depth 15.1m, Palmottu, Finland
	304/71.7	Uraninite, U-silicates	Drill hole 304, depth 71.7m, Palmottu, Finland
	346/209	Uraninite, U-silicates	Drill hole 346, depth 209m, Palmottu, Finland
2	Z497B	Torbernite	Zaire
	Z503B	Torbernite	Zaire
	Z546.2A	Soddyite	Zaire
	Z542A	Soddyite	Zaire
3	KAL/221/330	Calcite	Drill hole 330, depth 221 m, Palmottu, Finland
	KALS/214/301	Calcite	Drill hole 301, depth 214 m, Palmottu, Finland
	VKAL	Calcite	Unknown mixture
	KAO/221/330	Kaolinite	Drill hole 330, depth 221m, Palmottu, Finland
	VKAO	Kaolinite	Unknown mixture
	302/46-85	Calcite, chlorite	Drill hole 302, depth 46-85m, Palmottu, Finland
4	MG	Rock, granite boulder	Hämeenlinna, Finland
	211/325	Rock, granite pegmatite	Drill hole 225, depth 211 m, Palmottu, Finland
	346/103/JS	Rock, granite pegmatite	Drill hole 346, depth 103 m, Palmottu, Finland
	346/103/1	Rock, granite pegmatite	Drill hole 346, depth 103 m, Palmottu, Finland
	346/103/2	Rock, granite pegmatite	Drill hole 346, depth 103 m, Palmottu, Finland
	346/103/3	Rock, granite pegmatite	Drill hole 346, depth 103 m, Palmottu, Finland
5	1	Allanite	Brändö, Finland
	2	Allanite	Pyörönmaa, Finland
	3	Allanite	Varala, Finland
	4	Fergusonite	Pyörönmaa, Finland
	5	Monazite	Luumäki, Finland

To ensure that the separation of oxidation states was reliable quantitative the ion exchange procedure was checked with tracer solutions: ^{233}U solution for uranium oxidation state VI and ^{238}U solution for oxidation state IV. The ^{238}U solution was prepared from $^{238}UCl_4(s)$ by dissolving it in a mixture of 4.5 M HCl and 0.03 M HF. It was purified with respect to oxidation state just before use, by ion exhange. The $^{238}U(IV)$ tracer solution was found to contain a small amount of ^{234}U: in several measurements the average value of the $^{234}U/^{238}U$ activity ratio was 0.0013. The count rate of the $^{233}U(VI)$ peak was corrected for this. Oxidation state specific tracers were not used during later analyses: after testing of the procedure the separation of oxidation states was assumed to be reliable quantitative. A ^{233}U tracer was added as a yield monitor before

purification of the separated U(IV) and U(VI) fractions.

Water samples were filtered straight from the pumping device (a double packer system) in the field, through 0.45 µm membrane to acid solution. A protective gas flow was applied during the collection. The sample volume was generally between 0.5 and 1 litre, which was sufficient for the alpha spectrometry measurements.

Solid sample material was crushed to reduce the grain size. The pulverized sample was then leached with a mixture of 4.5 M HCl and 0.03 M HF under anoxic conditions in an ultrasonic bath to accelerate the dissolution. A mixture of HCl and HF acids was used for the dissolution of solid phases, as the decomposition is less drastic than when concentrated HF acid is used alone. The solubility of uraninite and other uranium-bearing minerals in HCl is greatly enhanced when small amounts of fluoride are added under anoxic conditions.[97]

3.2.2 Separation of oxidation states

Nd-coprecipitation for ground water and solid phases (**I,IV,V**)
The Nd-coprecipitation procedure is based on the coprecipitation of U(IV) with NdF_3 in acidic solution, while U(VI) remain in solution (Fig. 4). During the procedure, a nitrogen gas flow was kept bubbling in the sample vessel to prevent oxidation of uranium. Once the precipitate had settled the solution was passed through a membrane filter (0.45 µm pore size). After separation of the U(IV) and U(VI) fractions, ^{232}U tracer was added. The filter was wet ashed and the supernatant was heated to dryness; both fractions were then dissolved in concentrated HCl. The separated uranium fractions were further purified by ion exchange; strongly basic anion exchange resin was used for removal of disturbing alpha activities (e.g. Ra, Th). After the purification a few drops of $TiCl_3$ were added to the sample solution to reduce U(VI) to U(IV), which was coprecipitated with CeF_3 in acidic solution. The precipitate was mounted on a membrane filter (0.1 µm pore size) for alpha spectrometry.

Ion exchange for solid phases (**I,II,III,VI**)

In the presence of a small amount of HF, U(IV), in principle, is readily eluted through strong base anion exchange resin, while U(VI) is adsorbed on the resin (Fig. 5). The ion exchange column is regenerated with a mixture of 4.5 M HCl and 0.03 M HF acids. Sample solution was passed through the column where U(VI) was absorbed and U(IV) eluted. The absorbed U(VI) fraction was eluted with 0.1 M HCl. The procedure was performed under anoxic conditions in a protective gas flow. After the separation, the uranium fractions were treated separately. An internal yield tracer, ^{232}U, was added to both fractions, after which the solutions were heated to dryness and the residue was dissolved in concentrated HCl. The separated uranium fractions were further purified by anion exchange as described above. After the purification, $TiCl_3$ was added to the sample solution to reduce U(VI). U(IV) was coprecipitated with CeF_3 in acidic solution and the precipitate was mounted on a membrane filter (0.1 µm pore size) for alpha spectrometry.

3.2.3 Interference studies

Studies with ground water

A common method for determining total uranium concentration is Fe-coprecipitation: uranium is precipitated with $Fe(OH)_3$ from a solution of neutral pH.[98,99] This method was applied here to check the Nd-coprecipitation method, which uses a lower pH. ^{232}U tracer was used for yield determination. After precipitation the sample was filtered through 0.45 µm membrane, the membrane was wet ashed and the solution was heated to dryness. Uranium was dissolved in concentrated HCl and separated by anion exchange. After purification the preparate for alpha counting was prepared by Ce-coprecipitation.

Studies with solid phases (**II,III**)

The interferences of iron-containing minerals were tested by mixing pulverized minerals in amounts from 5 to 20 wt%, with uranium reference material. In the case of goethite the additions were continued up to 90 wt%. An ultrasonic bath was used to dissolve the uranium more effectively. The dissolution time was 1 hour, so the procedure was well within the bounds of the stability of the

reduced uranium in acidic conditions. The separation of oxidation states was done by ion exchange method.

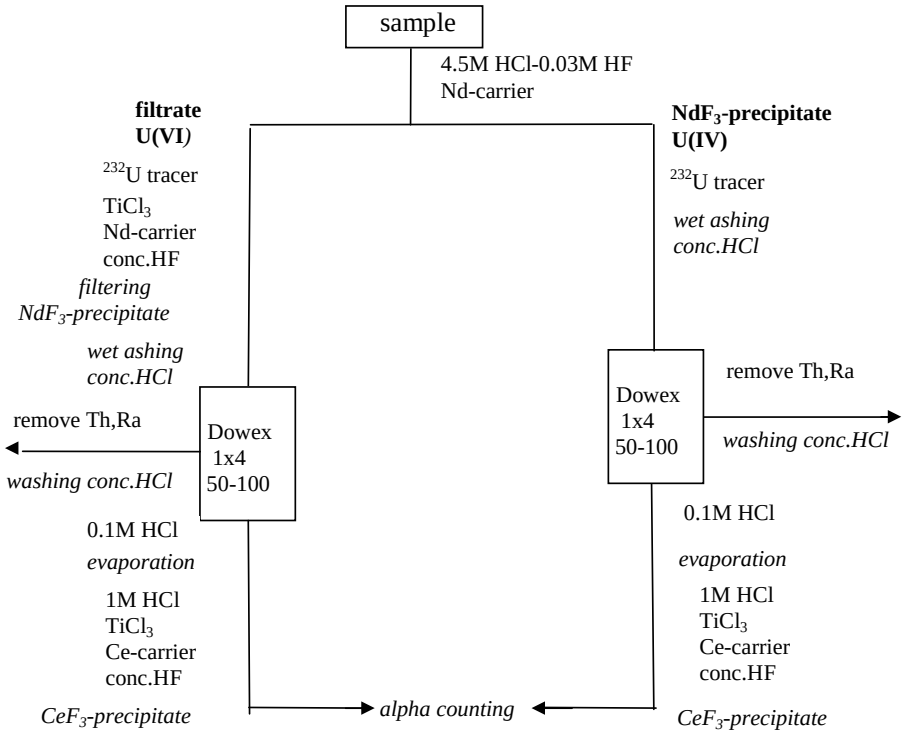

Figure 4. Scheme for separation of uranium oxidation states by Nd-coprecipitation method.

The behaviour of uranium oxidation states in natural samples containing iron was studied by adding dilute hydrazine-mineral acid solution to the sample. The dissolution and analytical procedure was the same as described above. Various carboxylic acids were tested with the reference material (DL-1a), and the one that performed best, PAA (polyacrylic acid), was employed in further studies. Pyrite, biotite and goethite were added to the reference material in an amount of 20 wt%, and PAA was added in different concentrations. The dissolution and analytical procedure was the same as described above.

3.3 Instrumentation

A conventional alpha spectrometry set-up was used in measuring the planchets containing the coprecipitated samples. Tennelec 256 measuring chambers and

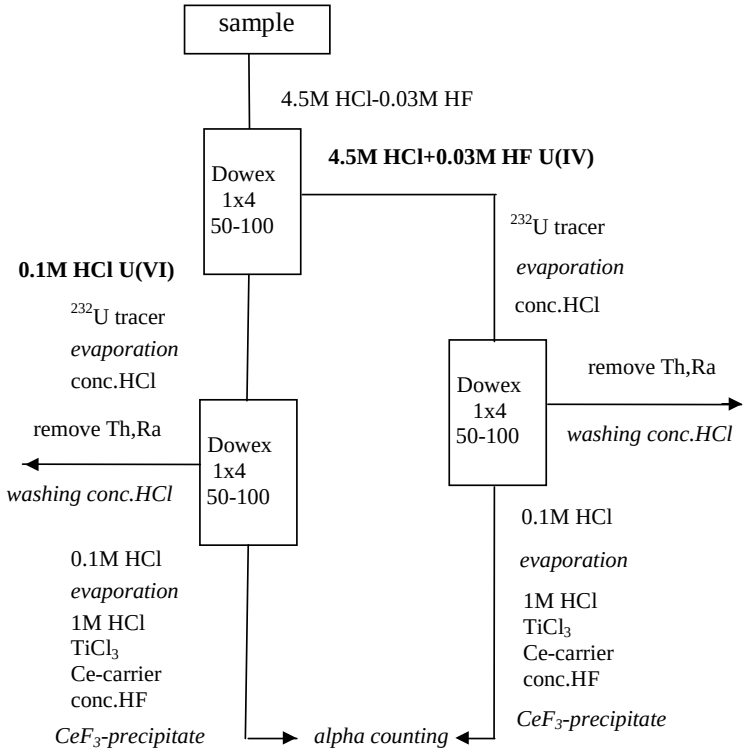

Figure 5. Scheme for separation of uranium oxidation states by ion exchange method.

silicon surface barrier detectors were employed. The pulses from each detector passed through a built-in amplification system (preamplifier, amplifier, biased amplifier) that provided signal conditioning and amplification. The signals were led to a 4096-channel analogue digital converter (ADC). A mixer router sorted signals from each detector into 256 channel regions of the analyser memory. The region of analysis for each sector in the multichannel analyser (MCA) was chosen to cover the energy region of about 3 to 8 MeV. A DMR-II microcomputer system guided the measurements. The spectra were further analysed with a commercial program for spectral analysis. Depending on

the detector set-up effectivities varied between 0.25 and 0.3 and resolutions between 50 and 100 keV. Background count rate was measured up to 0.002 cpm for ^{238}U. Energy calibration was based on ^{242}Pu, ^{243}Am and ^{241}Am alpha energies.

4. RESULTS AND DISCUSSION

4.1 Factors relevant to separation of uranium oxidation states (I)

When oxidation states are analysed by a chemical separation method, several factors need to be considered before the results can be regarded as valid. The following were evaluated in this study: reference material data, stability of uranium oxidation states, and selectivity, linearity, repeatability and comparability of the separation methods. Other factors, like robustness and reproducibility, were not investigated. In addition, results were examined and compared with values reported in the literature.

Reference material

No reference material for uranium oxidation states for water samples was available. Oxidation state specific tracers were used in testing of the method and, after testing the separation of oxidation states was assumed to be quantitative. Oxidation state specific tracers were not used in the actual analysis of ground water as there is a risk of oxidation during their preparation, transportation and handling in the field.

Suitable uranium reference material with certified oxidation state distribution data is not available for chemical determination of solid samples either. In their spectroscopic measurements, Sturchio et al.[40] used $[U(IV)P_5W_{30}O_{110}]^{11-}$ as U(IV) reference material, but this contains elements (P and W) likely to cause problems with the chemical methods used in this study. At first, synthetic UCl_4 was used to validate the methods. However, UCl_4 is highly active and reactive, and difficult to handle outside an inert atmosphere glove box. A more stable reference material for solid samples was sought, therefore.

A low-grade uranium ore material (DL-1a) was eventually chosen as reference and testing material.[93] Its oxidation state data were determined by two methods, which gave the same results within error limits: U(IV) was shown to represent 56% of the total uranium, which is an ideal oxidation state distribution for simultaneous examination of reduction and oxidation

changes. Since both oxidation states are present, only one reference material is required. In addition, the radioactivity level is suitable for the examination of environmental samples. The methods were further tested on minerals whose approximate oxidation states were known from mineralogical studies.

Stability of tetravalent uranium

Since it is essential that the U(IV)/U(VI) ratio should not change during the analysis, a stability test was carried out with tracer solutions containing 10^{-6} M of uranium in 4.5 M HCl and 10^{-5} M of uranium in a mixture of 4.5 M HCl and 0.03 M HF. The fresh solutions were stored in vessels with argon as a protective gas, and the U(IV)/U(VI) ratio was measured as a function of time. Only negligible decrease was observed during the time required to dissolve and separate U(IV). The addition of fluoride increases the stability of U(IV).[97]

The rate of oxidation of U(IV) in pure acid solution (homogeneous) can be described by a first order dependence on the concentration of U(IV) according to the equation

$$\frac{d[U(IV)]}{dt} = -k_{ox}[U(IV)] \qquad (7)$$

where [U(IV)] is the concentration of U(IV) species and k_{ox} is the apparent first order reaction constant ($k_{ox} \cong \ln 2/t_{1/2}$, where $t_{1/2}$ is the half-life time of the reaction. The experimental points were fitted by the method of least squares for exponential curve fit. The half-life time for the acid mixture of 4.5 M HCl and 0.03 M HF in anoxic conditions and uranium concentration of 10^{-5} M was 292 hours. This is equivalent to oxidation of less than 1% of uranium during the time of analysis.

For dilute HCl solutions under ambient atmospheric conditions Röllin and Eklund[67] found that the reaction rate of uranium oxidation was independent of the U(IV) concentration in the range $4x10^{-8}$ – $4x10^{-11}$ M. The apparent first order reaction constant for the oxidation of U(IV) was found to depend on the dissolved oxygen and hydrogen ion concentrations. In a study of the stability of U(IV) in 4.5 M HCl at 10^{-5} – 10^{-8} M concentrations of uranium, however,

Hussonois et al.[16] found the reaction rate to depend on uranium concentration. These opposing results indicate the difficulties encountered in experimental set-ups. In natural samples there may be further complications in the presence of elements that affect the stability of the different oxidation states of uranium. Both sets of results mentioned above, it should be noted, are for pure synthetic solutions and not, therefore, strictly valid for complex natural systems.

Selectivity

The selectivity of the ion exchange procedure was checked with tracer solutions: ^{233}U solution for uranium oxidation state VI and ^{238}U solution for oxidation state IV. The separation of the oxidation states is easily seen in the elution curves shown in Figure 6. The alpha spectra of uranium isotopes in different oxidation states are presented in Figure 7. The fractions corresponding to specific oxidation states slightly overlap: 2.5% of U(IV) is present in the U(VI) fraction, and 1.7% of U(VI) is present in the U(IV) fraction. Hussonois et al.[16] obtained less than 5% of U(IV) in U(VI) fraction and less than 1% of U(VI) in U(IV).

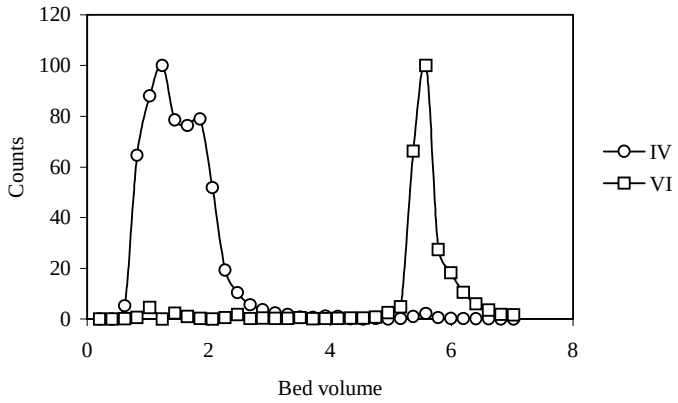

Figure 6. The separation of uranium oxidation states by ion exchange studied with tracers ^{238}U(IV) and ^{233}U(VI). Strong base anion exchange resin Dowex 1x4 (50-100 mesh) was used. The y-count scales have been normalized by peak height. (**I**)

The separation efficiency was tested by changing the HF acid concentration. At low concentrations (<0.1 M HF), the U(IV)/U_{tot} ratio was more or less constant. At higher concentrations, the adsorption of U(VI) declined and some U(VI) was

eluted with the U(IV) fraction. The weaker adsorption at higher concentration is due to the formation of fluoride uranium complexes carrying a positive charge.[17]

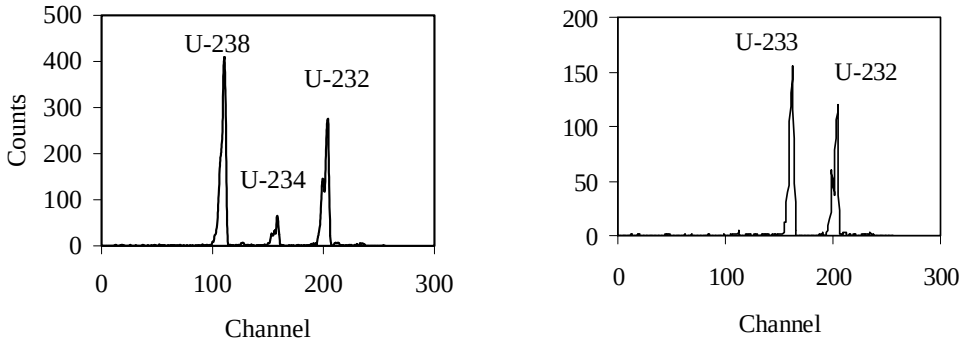

Figure 7. The alpha spectra of ^{238}U(IV) (on the left) and ^{233}U(VI) (on the right) from tracer tests. ^{232}U tracer was used for the yield determination of the separated fractions of oxidation states. (**I**)

Leskinen[63] has reported a slight overlapping for the Nd-coprecipitation method: U(IV) fractions contained 2% of U(VI) and U(VI) fractions 1% of U(IV). Corresponding values were obtained in this work. Andersson[11] found as much as 5-20% crossover but explained the high value as due in part to experimental difficulties, such as oxidation of the tracer before separation.

Linearity and detection limit

The coprecipitation and ion exchange methods are suitable for the analysis of uranium oxidation states over a wide range of uranium contents, isotopic ratios and oxidation state distributions. In tests with natural ground waters the Nd-coprecipitation method was found to be linear for uranium concentrations from 0.01 to 9 nM and isotopic ratios from 1.1 to 3.8. In the case of solid samples the coprecipitation and ion exchange methods were linear for oxidation state distributions varying from 5 to 75% of U(IV)/U_{tot}.

The detection limit for the Nd-coprecipitation and ion exchange methods was

obtained with the Curie formula (Lower Limit of Detection).[100] The detection limit was 0.4 mBq of uranium in either U(IV) or U(VI) state for 6000 min counting time. This limit is valid for a one-litre ground water sample. The detection limit depends on detector background, sample size and yield of separation method and may be improved by longer counting time and larger sample size.

Repeatability

The repeatability of the two methods was tested with reference material DL-1a. From each dissolved DL-1a sample, subsamples of about 0.05 g were taken for analysis. The mean value of U(IV)/U_{tot} for 12 replicates was (56 ± 8) % for the ion exchange method and (51 ± 9) % for the coprecipitation method. The standard deviation was 1 sigma. The repeatability would be improved with larger samples and longer measuring time. One population t-test did not reveal any significant difference from the mean for either method ($t = -0.111$, $p = 0.914$).[101]

Random errors were assessed through use of parallel samples. These samples represented a longer time interval than those in the repeatability test. Relative random deviation for U(IV)/U_{tot} % was 13% for Nd-coprecipitation and 10% for ion exchange method.

Comparability

In determination of the total uranium concentration, the separation of uranium from ground water was performed by Nd- and Fe-coprecipitation methods. Incomplete or disturbed coprecipitation of uranium would appear as lower activity and difference in isotopic ratio. Chemically different types of water were analysed, with the results shown in Table 6. Correlation for the concentration was 0.999 and for the isotopic ratio ($^{234}U/^{238}U$) 0.990. The paired t-test revealed no significant difference at 0.05 level ($t = 0.107$, $p = 0.918$) between results of the two methods.[101]

Table 6. ^{238}U activity concentrations and $^{234}U/^{238}U$ activity ratios in ground waters from the Palmottu study site determined by Nd-coprecipitation and Fe-coprecipitation methods. Values are the averages of two parallel determinations with one sigma standard deviation.

Drill hole	Depth (m)	Water type	Nd ^{238}U(mBq/l)	Nd $^{234}U/^{238}U$	Fe ^{238}U(mBq/l)	Fe $^{234}U/^{238}U$
385	403-409	Na-Cl	3.62±0.26	2.79±0.23	4.61±0.34	2.84±0.25
357	165-171	Na-Ca-HCO_3-Cl	67±6	3.82±0.42	73±5	3.64±0.33
318	50-80	Ca-HCO_3-SO_4	1020±50	1.54±0.11	1020±40	1.53±0.08
324	175-200	Na-Ca-HCO_3-SO_4	414±21	1.20±0.09	471±16	1.14±0.06
346	240-246	Na-SO_4	18.3±1.9	3.36±0.41	15.5±1.8	3.48±0.49
387	304-339	Na-Cl-SO_4	15.6±0.8	2.13±0.13	15.4±0.9	2.07±0.15
384	57-94	Ca-Mg-HCO_3	1140±60	1.06±0.08	970±70	1.15±0.11
302	80-131	Ca-Na-HCO_3	2640±110	1.96±0.12	2586±98	1.90±0.10

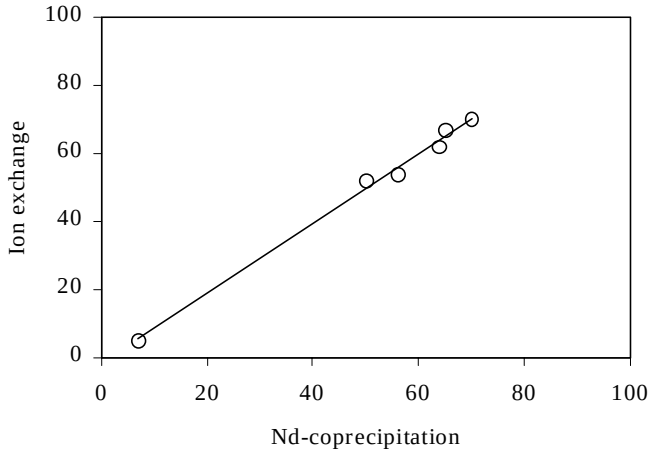

Figure 8. Comparison of Nd-coprecipitation and ion exchange methods used for solid samples. The values are U(IV)/U_{tot}(%).

The ion exchange and Nd-coprecipitation methods were compared for solid samples. Figure 8 shows the results as U(IV) percentages of U_{tot}. There is a good correlation, 0.994, between the two methods. The one-way analysis of variance test (ANOVA)[101] showed no significant difference at 0.05 level ($F = 0.001$, $p = 0.981$).

4.2 Disturbing elements in water sample

All water samples in the study were analysed by Nd-coprecipitation method where the uranium coprecipitates with NdF_3. During precipitation, several ions compete for fluoride and the available coprecipitation sites. In general, a high salt concentration in water reduces the yield of separation and prevents reliable quantitative separation of uranium oxidation states by this method.

The EC and chloride and iron concentrations were used as indicator factors for preliminary identification of suitable samples for analysis by the Nd-coprecipitation method. At first, as the limiting value for chloride the chloride concentration of sea water (~20g/l[102]) was used. However, the analysis of several ground waters show that separation may be incomplete even with a chloride concentration of about 4 g/l. The probable cause of the interference was the high concentration of calcium in Ca-Na-Cl type of waters. Duff and Amrhein[68] report that over 0.4 g/l of calcium can have serious effects.

No interferences were observed during coprecipitation in samples from drill holes 385 at depths 217-223m, 403-409m and 346 at depth 122-128m, which contained the highest measured concentrations of Al, Mg, Ca and Cl (0.1, 7.68, 87.3 and 855 mg/l respectively). The concentration of calcium is below the value in a sea water sample that was successfully analysed for $U(IV)/U_{tot}$ by Anderson.[11] A check for disturbances during the precipitation was made by another co-precipitation method where iron was used as carrier. The results for various types of waters analysed by Nd- and Fe-coprecipitation methods are given in Table 6. The yields and spectra were in all cases very good: if there had been some disturbance during the separation, the total uranium concentrations and isotope ratios obtained by the two methods would not have agreed.

In samples where there is incomplete coprecipitation of uranium, this can taken into account by using yield tracers for the two oxidation states.[11,26] This tends to be a complex operation, however, with a risk of oxidation of the tracer before use. Careful attention is required to apply the right separation method even in total uranium determinations. It is recommended, therefore,

that complex water samples be analysed by another more suitable method, for example by ion exchange method.

4.3 Disturbances in the dissolution of solid phases (II)

In the analysis of a solid sample, problems may begin right at the beginning, at the dissolution of the sample. Redox reactions may occur if any element capable of shifting the redox potential of the solution is acting as reductant, oxidant or catalyst. Redox reactions triggered by these elements could cause a change in the uranium oxidation state distribution,which is not acceptable.

The main concern is iron with its two oxidation states, II and III. Study was made of the effect of interfering iron in determination of the oxidation states in a solid sample. Natural iron minerals, common in rocks – pyrite, biotite, hornblende, goethite and chlorite (see Table 2, sect. 3.1) – were investigated by addition in increasing amount to reference material DL-1a.

As the amount of pyrite was increased, an increasing amount of uranium in solution changed to reduced state; increasing amounts of goethite in turn caused an increasing amount to change to oxidized state (Fig. 9). The interferences of the silicates fell between those of pyrite and goethite. The results indicate that a wide range of common rocks with less than 20 wt% of iron-containing minerals can be reliably analysed for uranium oxidation state by chemical methods. Rocks containing pyrite heterogeneously distributed cannot, however, be analysed in this way.

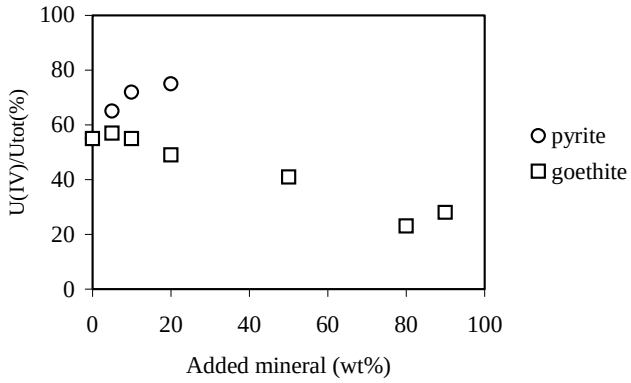

Figure 9. U(IV)/U_{tot} ratios measured as a function of pyrite (Fe^{+2} 100%) and goethite (Fe^{+3} 100%) added to reference material DL-1a. (II)

The dissolution of total uranium was investigated with use strong mineral acids in oxidizing conditions. Uranium was totally dissolved from all samples except from monazite. In the case of monazite, the oxidation state distribution was calculated by assuming that the fraction dissolved in mineral acid was the oxidized form of uranium, while the uranium remaining in the mineral was the reduced uranium.

4.4 Detecting and minimizing interferences (III)

As noted in section 4.3, pyrite and goethite caused severe disturbances to U(IV)/U_{tot} ratios. Complex geological materials thus require modifications to the method used to determine uranium oxidation states. A number of reagents have been tested to prevent interference from iron. These include hydrazine and polyelectrolyte carboxylic acids, which mask the iron while leaving the uranium uncomplexed.

Use of hydrazine as holding reductant did not affect the oxidation states of dissolved uranium in materials that did not contain iron or other interfering elements in high concentrations. Use of a holding reductant allows the identification and rejection of sample materials that are too complex for analysis by this method at this stage without further improvements to the

method and understanding of the underlying reactions. The use of hydrazine gave values that were either the same or higher than those obtained with acid alone. Until the ideal redox buffer is found, hydrazine can be considered a reasonable indicator of undesired redox reactions.

Organic carboxylic acids were studied as a means of minimizing the effects of iron in the determination of oxidation states. The acids (see Table 3) can be classified as normal, polymeric and copolymeric. First the acids were tested on the reference material DL-1a to confirm that they themselves did not change the oxidation distribution (Table 7). Only AA gave a results that was statistically different from the value for DL-1a alone, but as PAA seemed to be the most useful considering the molecular size it was chosen for study of reference material to which iron minerals were added (see sect. 4.3). Since the samples contained excess of iron relative to uranium, it was assumed that the iron ions utilize most of the complexation capacity of PAA and other heavy trace metals the rest.[103] PAA forms complexes with other cations so that uranyl ions are shielded by the macromolecular structure from redox reactions.

Table 7. Organic carboxylic acids studied and U(IV)/U_{tot} ratios obtained in testing with reference material DL-1a. The corresponding value for DL-1a alone is 56 ± 8.

Abbr.	Acid	U(IV)/U_{tot} (%)
PAA	Polyacrylic acid (Na-salt)	57 ± 3
LA	Lactic acid	66 ± 4
PAMA	Poly(acrylic-co-maleic acid) (Na-salt)	55 ± 3
PA	Propionic acid (Na-salt)	55 ± 3
AA	Acrylic acid	75 ± 4

Larger additions of iron mineral were found to change the oxidation state distribution and it was necessary to increase the acid concentration. The oxidation state distribution as a function of PAA concentration was studied with DL-1a reference material and biotite and pyrite as added mineral. The results are shown in Figure 10. In the case of both biotite and pyrite, a 2.5% concentration of PAA was able to eliminate the oxidation state changes of 20 wt% mineral additions. These results and observations are promising and can be exploited in the determination oxidation states of complex samples. The application of PAA makes it possible to analyse samples such as fracture

coatings and rock samples that may contain considerable amounts of iron compounds.

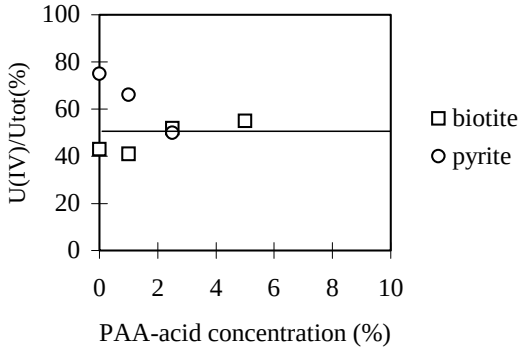

Figure 10. Oxidation state distribution as a function of PAA concentration using the reference material DL-1a and 20 wt% content of biotite or pyrite. The straight line represents the value of $U(IV)/U_{tot}$ (%) obtained for the reference material without added PAA or mineral. (**III**)

4.5 Application of methods

4.5.1 Ground waters (IV,V)

The ground water samples represented different types of ground water, from both oxic and anoxic environments. The oxidation states of the analysed samples are shown in Table 8 together with the measured pH and Eh values. Some modelled Eh values are included. The computer code PHREEQE was utilized together with OECD/NEA and CHEMVAL4 databases.[50,51]

As expected, uranium was found to exist in U(VI) oxidation state in drill holes with positive or slightly negative Eh value. In drill holes 302 and 324 the amount of dissolved oxygen (>0.1 mg/l) indicated oxidizing conditions and the measured Eh values correlated well with the calculated Eh values. If an uncertainty of ±30 mV is assumed, corresponding to the average fluctuation reported[8] during field sampling, there is a difference in the measured and calculated values only for sample 346/240-246m. Samples at depths of 122-128m and 240-246m in drill hole 346, showed highest U(IV) content, 60% and 93%, respectively.

Although the differences in the physico-chemical properties were slight, the parallel samples 346/122-128 displayed highly dissimilar uranium-redox state characteristics. These samples were from the redox boundary and at the redox boundary, minor changes in environmental conditions are heavily reflected in the oxidation data distribution, since the stability fields of different species overlap in a narrow area. Study of the measurements and the thermodynamic stability boundaries between uranium species in ground water showed that uranium minerals, especially uraninite, could be important redox buffers.

In model experiments of Bruno et al.,[52,56]a good correlation was found between the redox potential of solid phases assuming equilibrium between UO_2(c) and U_3O_7 and that found with the model program HALTAFALL based on the INPUT/SED/PREDOM code package in conjunction with the SKBU1 database. The stability constant value log K for the formation of $U(OH)_4$ (aq) was –5.13, which is close to the values used here in the modelling of equilibrium between water phases. Use of the Nernst equation to calculate the prevailing redox potential assumes the existence of thermodynamic equilibrium. The question of the existence of a thermodynamic equilibrium in Palmottu ground water was considered by Bruno et al.[52] According to them, the time to reach equilibrium can be assessed by applying the concept of characteristic reaction times of slow processes and comparing the reaction times with the residence times in the system under consideration. Since residence times were long and the ground water system was close to the uranium mineralization, the thermodynamic approach to model the measurements of the redox potentials at Palmottu was considered to be appropriate.

Since the water was filtered through a filter of relatively large pore size (0.45 μm) before separation of oxidation states, any colloidal material in samples would appear in the U(IV) fraction. Vuorinen and Kumpulainen[104] attempted characterizations of water from the same drill holes (324, 346) concentrating the colloidal phase from the ground water by tangential ultrafiltration and carrying out ICP-MS measurements (results in Table 9). No direct evidence was obtained for uranium in the colloids, perhaps due to low uranium content or insufficient sensitivity of the method. The present research (paper **IV**)

showed that there is only a minor amount of uranium in colloids of these ground waters.

Table 8. Results for the analysis of ground water samples from the Palmottu area. Experimental values are the averages of two parallel determinations with one sigma standard deviation. The calculated values were obtained by two different approaches: in this work the equilibrium was modelled between species in ground water (**IV,V**) and in Bruno et al.[52] it was modelled for solid phases assuming equilibrium between $UO_2(c)$ and U_3O_7.

Drill hole	U(IV)/U_{tot} (%)	pH	Eh (mV)	$Eh_{calc}^{IV,V}$ (mV)	Eh_{calc}^{52} (mV)
302/90-95	2.8±0.2	8.42	-55	-40	-45
324/95-101	5.5±0.2	6.87	+55	+70	-
346/65-71	6.6±0.3	8.05	-11	-40	-28
346/122-128	6.2±0.6	8.40	-70	-70	-45
346/122-128	60±32	8.40	-80	-110	-45
346/240-246	93±7	9.05	-92	-165	-88
348/200-225	7.2±0.7	8.82	-70	-71	-72

Table 9. Uranium concentration U(µg/l) in ground water in different size fractions.

Drill hole	Paper **IV**		Vuorinen and Kumpulainen[104]		
	>0.45µm	<0.45µm	<0.45 µm	2-500nm	<2nm
324/95-101	0.8	63.5	76.13	91.5	69.87
346/65-71	0.14	105.7	102.0	108.9	104.5
346/122-128	0.03-0.05	9.6-10.0	10.1	12.5	10.3
346/240-246	0.03	1.6	1.0	1.1	1.1

Subsequent measurements in ground waters at Palmottu have confirmed that the overall concentration of colloids is low.[95]

Since the amount of the colloidal phase was not determined in the samples of the present study, there is no direct evidence that the measured U(IV) was indeed in solution. The measured U(IV) concentration was nevertheless low, as low as $2 \cdot 10^{-8}$ M, in agreement with the sparing solubility of reduced uranium. The carbonate concentration decreased at deeper depth, which favours the U(IV) form. Also the inorganic salt concentration, which was higher in the deeper sample 346/240-246, may hinder the formation of colloids.

High values of reduced uranium in deep ground waters in Finland filtered through 0.45 µm filter have been reported by Pilviö[27]; values of $U(IV)/U_{tot}$ were as high as 86%. Neither the amount of uranium bound in colloids nor the concentration of colloids was given, however. Zeh et al.[105] found that over 75% of the natural uranium in the Gorleben ground water in Germany was colloid-borne. The amount bound to dissolved organic compounds was over 90%. Calculations predicted less than 1% of U(VI) to be in humic colloids. These findings, together with the low ground water Eh at Gorleben, suggested that the uranium was in tetravalent oxidation state.

The interpretation of measured redox potentials is complicated by the weak mineralization of most natural waters, poisoning of the platinum electrode surface or the influence of several redox systems being main difficulties.[8] The reliability can be improved by measuring with several electrodes at the same time and comparing their results. However, more quantitative information on formation constants for U(IV) hydrolysis and carbonato species is required to achieve accordance among model results and laboratory and field measurements.

4.5.2 Solid phases (I,III,VI)

The analysed solid phases represented different types of materials, different uranium oxidation state distributions and different uranium concentrations (Table 10). The solid materials can be divided into five groups: 1) the synthetic uranium compound and uraninites, which represent the most reduced form of uranium, 2) secondary uranium phases, which represent the most oxidized form of uraninite, 3) fracture coatings and 4) rock materials showing a more varied oxidation state distribution, 5) uranium-bearing minerals representing samples in which uranium was assumed to be in reduced state from geological classification of the uranium minerals.[106]

1) Synthetic uranium compound and uraninites

The synthetic UCl_4 was expected to be totally in U(IV) oxidation state. The measured value of 90% can be considered in agreement with this since some

oxidation of the surface likely occurred during storage.

The uraninite UO_{2+x} ($0<x<0.25$) sample A9645 could have being similar to the samples analysed by Ordonez Regil et al.[58] (ion chromatography) and Kobashi and Tominaga[13] (precipitation). The results obtained in the present study are similar to their findings of 51% and 55%. Some alteration products on the surface were detected in the mineralogical study and visually, which may indicate that the whole sample was partially altered and oxidized. On the other hand, part of the present U(VI) may be original since uraninite can crystallize as a complex U(IV,VI) oxide even under reducing conditions.[107]

The uranium is generally in lower oxidation state in pegmatitic uraninite, such as the uraninite samples from Palmottu, than in vein and sedimentary uraninite.[42] The amount of reduced uranium in the drill core sample 304/71.70 could correspond to $UO_{2.30}$ or higher stage. The $UO_{2.25}$ or $UO_{2.33}$ stage is generally the most oxidized form of uraninite found in contact with moderately oxidizing waters. The results of the present study lie between these, while XPS studies[95] on uraninites from Palmottu give values ranging from $U_{2.21}$ to $U_{2.43}$. $U(IV)/U_{tot}$ percentages were 65, 70, 64% in this study compared with the corresponding XPS results of 61, 79, 63%. Our value for sample 304/71.7 was slightly lower than the value found by XPS, while the present and XPS values of other samples were within error limits.

The results obtained by the ion exchange and XPS methods are not exactly the same because the XPS study was not carried out on the same mineral grains; moreover, the limitation of the XPS method to surface analysis may give different results from a method in which a larger amount of material is analysed. Sunder et al.[73,108] determined, by XAS, the oxidation states in a high-grade ore zone at Cigar Lake in Canada (uranium ore minerals: uraninite and coffinite $USiO_4$) and found U(IV) $/U_{tot}$ to range between 78 and 86%.

2) Secondary uranium phases

Soddyite $(UO_2)_2SiO_4 \cdot 2H_2O$ and torbernite $Cu(UO_2)_2(PO4)_2 \cdot 8\text{-}12H_2O$ are the end members of the oxidation of uraninite. The uranium oxidation state

distribution of these solid phases is therefore expected to be in favour of U(VI). The U(IV)/Utot values of 5.8-8.7% obtained in this study are in good agreement with this.

3) Fracture coatings

In general, the calcite infillings at Palmottu contain considerable amounts of impurities from the wall rock. Locally the calcites ($CaCO_3$) are densely laminated or exhibit reactivation growth textures reflecting the complex evolution of the fracture infillings. Some of the fractures are closed and some open. The samples are thick and thus may represent several precipitation cycles, and ground water conditions may have varied during these cycles.[95] It is difficult, therefore, to predict the oxidation state distribution of these samples. All the analysed fracture coatings were partially oxidized.

Both calcite and kaolinite ($Al_2Si_2O_5(OH)_4$) were identified in sample 221/330, and they gave similar U(IV)/U_{tot} values, indicating that the developed method is effective. Sturchio et al.[40] employing XAS found that, under reducing conditions, U(IV) can substitute for Ca(II) in calcite samples. Cui and Eriksen[83] found the uranium to be partially oxidized, 20-30% for U(IV)/U_{tot}, in Fe(II)-chlorite fracture coatings from different drill cores at Palmottu. They used the ion exchange method that was developed in this study. The results were explained in terms of oxidation occurring after formation.

4) Bulk rock

The uranium oxidation state distribution in the rock samples was not known, but high U(IV)/U_{tot} ratios describe the buffer capacity of the bedrock minerals in the area. Exceptionally, geological interpretation suggest that the uranium in sample MG should be mostly in U(VI) state,[109] and the measured value supports this. However, MG, as well as samples 211/325 and 346/103/JS, gave clearly higher U(IV) results when they were treated with hydrazine mask, which suggests that the original results are not necessarily valid and wider error limits should be assumed. Sample 346/103/JS was collected from close to a fracture surface affected by oxidizing ground water. The samples 346/103/1-3 were from deeper rock and the values were indicative of less

oxidizing conditions.

Table 10. Values of $U(IV)/U_{tot}$ for analysed solid materials expressed as averages of two parallel determinations with one sigma standard deviation (uranium oxidation states). The values in parenthesis are XPS results reported in Blomqvist et al.[95]

Type	Sample	Material	$U(IV)/U_{tot}$ (%)
1	UCl_4	Synthetic	90±5
	A9645	Uraninite	50±2
	DL-1a	Uraninite, brannerite	56±8
	304/15.1	Uraninite, U-silicates	65±4 (61)
	304/71.7	Uraninite, U-silicates	70±4 (79)
	346/209 (211)	Uraninite, U-silicates	64±3 (63)
2	Z497B	Torbernite	7.4±0.3
	Z503B	Torbernite	5.8±0.3
	Z546.2A	Soddyite	8.7±0.4
	Z542A	Soddyite	8.4±0.4
3	KAL/221/330	Calcite	36±3
	KALS/214/301	Calcite	49±3
	VKAL	Calcite mixture	15±10
	KAO/221/330	Kaolinite	31±2
	VKAO	Kaolinite mixture	48±14
	302/46-85	Calcite, chlorite	36±2
4	MG	Rock, granite	13±2
	211/325	Rock, granite	64±5
	346/103/JS	Rock, granite	40±5
	346/103/1	Rock, granite	77±7
	346/103/2	Rock, granite	74±6
	346/103/3	Rock, granite	68±5
5	1	Allanite	33±1
	2	Allanite	35±1
	3	Allanite	43±2
	4	Fergusonite	5.9±0.5
	5	Monazite	93±5

5) Uranium-bearing minerals

Uranium oxidation states were determined in three Ce-allanites $(Ce,Ca,Y,Mn)_2(Fe,Al)_3Si_3(O,OH,F)_{13}$, fergusonite $(Y,Ce)(Nb,Ta)O_4$ and monazite $(Ce,Th,Nd,La)PO_4$ from granitic pegmatites in Finland. Following Smith Jr.,[106] the metamict allanites were assumed to be originally U(IV) minerals. In this study they were found to be significantly oxidized, with $U(IV)/U_{tot}$ values ranging from 33 to 43%. Oxidation states have not earlier been reported for allanites, so the original oxidation state distribution is not known. Additional research is needed to confirm the oxidation state distribution and also the contribution of metamictic processes to the oxidation of uranium.

Uranium in the metamictic fergusonite was totally oxidized; the value for $U(IV)/U_{tot}$ was just 6%. The low ratio is in accordance with the altered structure seen in a microprobe profile, probably due to hydration. Since the allanite and fergusonite were from the same location, the lower level of oxidation in allanite than in fergusonite may reflect greater stability of allanite than of fergusonite. As expected, uranium in the monazite was totally in reduced form, $U(IV)/U_{tot}$ was 93%.

5. CONCLUSIONS

Chemical speciation studies of uranium provide an understanding of the behaviour of uranium in the environment, necessary for safety assessments of nuclear waste management and for remediation of areas contaminated by the nuclear fuel cycle and agricultural activities. Analysis of the oxidation states of uranium is demanding owing to the easy contamination with oxygen, the low concentration of uranium in environmental samples and the complexity of geological matrices.

A method of analysis based on Nd-coprecipitation was tested for determination in the field of uranium oxidation states in ground waters of different type and with wide range of uranium concentrations. High concentrations of iron and calcium and high salinity of water disturb the analysis and another separation method, such as ion exchange, is recommended for these samples. In granitic bedrock, uranium in ground water was found in oxidized form in the upper part of the bedrock (0-101m) and in reduced form in the deeper part. A good correlation was obtained between the measured redox potentials and model values. Study of the measured values and thermodynamic stability boundaries between uranium species in ground water indicated that uranium minerals, especially uraninite, could act as redox buffers.

A chemical separation method was developed for natural solid materials. The method is based on ion exchange from an acid mixture of 4.5 M HCl and 0.03 M HF. Comparison with Nd-coprecipitation, showed the ion exchange method to be effective. It was successfully applied to the analysis of several geological materials, with results similar to those reported in the literature.

Heterogeneous samples, such as bulk rock and fracture coatings, may contain iron-rich side material, that is not in equilibrium with uranium. Common iron-bearing minerals were tested for their ability to interfere with the dissolution of samples before separation of oxidation states. It was found that minerals such as biotite, hornblende and chlorite do not disturb the analysis of uranium oxidation states up to 20 wt%, which means that the ion exchange method can

be applied to samples containing less than this amount. Pyrite and goethite, which contain considerably more iron, produce severe interference in the analysis of heterogeneous samples. Testing of several carboxylic acids showed polyacrylic acid (PAA) to be the most useful in minimizing the interference due to iron. PAA increased the reliability of results by preventing changes in the oxidation state distribution in samples containing pyrite. An equally efficient compound was not found for goethite (iron hydroxide).

Nd-coprecipitation and ion exchange method are valid and reliable methods for the analysis of uranium oxidation states in a variety of samples, both solutions and solids. Ground waters, uranium minerals, fracture coatings, bulk rock samples and uranium-bearing minerals were successfully analysed, providing new information on the chemical speciation and behaviour of uranium in these materials. The methods are suitable tools for studying oxidation/reduction mechanisms in geochemical processes.

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